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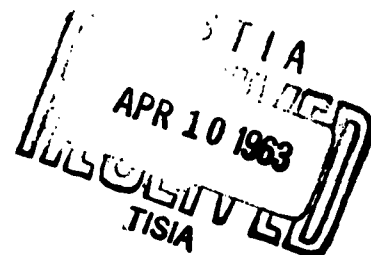
THE ADSORPTION MECHANISM OF THE ACTION OF CERTAIN ACID
CORROSION INHIBITORS

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- USSR -

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THE ADSORPTION MECHANISM OF THE ACTION OF CERTAIN ACID
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-USSR-

[Following is a translation of an article by H. H. Lysenko and O. S. Afanas'yev of the Dnepropetrovsk Metallurgical Institute and Melitopol'sk Pedagogical Institute, presented by Academician U. K. Delimars'kiy, in the Ukrainian-language periodical Dopovidi Akademiyi Nauk Ukrayins'koyi RSR (Reports of the Academy of Sciences of the Ukrainian SSR), No. 8, Kiev, 1961, pages 1049 - 1051.]

The introduction of inhibitors into a corrosion-active solution truly changes the properties of the metal surface if the inhibitor particles are adsorbed [1]. For this reason the question of the ability of the inhibitor to be adsorbed is very important in determination of the mechanism of action of additives as inhibitors.

We studied the effect of hexamethylenetetramine as the inhibitor on the properties of the surfaces of steel and mercury in a sulfuric acid solution. The main results and methods have been described before in [2 - 4]. It was proven that active particles in the solution are those of hexamethylenetetramine and of the products of its acid decomposition

and electroreduction: amines of various compositions and structures, formaldehyde, ammonia or all together, in other words "hexamethylenetetramine complex". Thus, hexamethylenetetramine is classified by us in the mixed class of inhibitors of the cation-molecular type. The inhibiting action of hexamethylenetetramine is explained by changes of properties of the sulfuric acid solution: increase in pH and accumulation of various substances of the hexamethylenetetramine complex depending on the pH of the solution. In addition, the adsorption of hexamethylenetetramine on the surface of metal changes the structure of the double layer and also changes the active unscreened corrosion surface. The last function of the hexamethylenetetramine is much more important in the concentrations of acids used in pickling and manufacturing.

Our electrocapillary measurements showed that all investigated concentrations of hexamethylenetetramine shift the zero charge potential of mercury in H_2SO_4 to the positive side. The magnitude of shift in 1N H_2SO_4 is: for concentration 1 g/l -- 10 mv; for 10 g/l -- 50 mv; for 40 g/l -- 100 mv (very similar values were obtained by us for 0.2 N H_2SO_4).

The specific adsorption on the positively charged surface is also evident for all solutions of hexamethylenetetramine. It is observed during shift of the potential

to the positive side of the potential of the zero charge for solutions with 1 and 10 g/l of hexamethylenetetramine by 50 - 100 mv, and for a solution with 40 g/l by 200 - 250 mv (this is only part of our data).

The stationary potential of the corroding steel, covered with scale and steel without scale, depends on the concentration of hexamethylenetetramine and on the concentration of acid. It may be shifted either in the positive or in the negative direction with respect to the stationary potential in the same solution. Such a characteristic effect of hexamethylenetetramine on the magnitude of the stationary potential causes desorption of the individual component parts of the hexamethylenetetramine complex during anodic polarization of steel.

In H_2SO_4 solution containing 1 - 10 g/l of hexamethylenetetramine the values of stationary potential and of the zero charge potential are very close. Thus, in anodic polarization at 30 - 50 mv the desorption potential is reached for the cation part of the hexamethylenetetramine complex. The anodic polarization curves in this case have characteristic desorption slopes. The anodic curves for solutions which contain only formaldehyde do not have such slopes. However, it is only the cation fraction of the hexamethylenetetramine

complex which is desorbed and not the molecular fraction.

In 0.2 N H_2SO_4 which contains 40 g/l of hexamethylenetetramine the stationary potential (-420 mv) is much more negative than the zero charge potential (-330 mv), therefore, under these conditions the desorption potential is not reached.

At all values of the stationary potential a specific adsorption of the cation fraction of the hexamethylenetetramine complex is observed at the anode. The electrostatic adsorption can take place in that case when the stationary potential is more negative than the potential of the zero charge. The combination of the polarization investigations with steel and polarographic and electrocapillary investigations with mercury, along with the simultaneous registration of current in the electrocapillary apparatus circuit proved to be highly effective for determining the mechanism of the inhibition action.

The mechanism of the action of the additives to solutions should be divided into two groups:

1) Additives which during polarization do not change their chemical nature and at definite values of the potential are desorbed from the surface of metal.

2) Additives which are adsorbed at definite values of the potential and are oxidized or reduced. The effectiveness of such additives as inhibitors is lowered at those potentials

at which electrochemical processes take place.

Cathodes and anodes may adsorb cations, anions and molecules. Their adsorption is due to the action of electrostatic and specific forces or generally by one type of forces. In polarization with external current the electrostatic effect on the adsorption of particles from solution is freely regulated. In this the potential of the electrode either approaches or is further removed from the potential at which the action of these specific forces is predominant. The obtained results for the additives of the molecular and cationic type which were obtained in our investigations and also the analysis of the literature data on the additives of the anionic type [5, 6] permitted the establishment of a number of characteristic signs for the adsorption processes and to establish the relationship between the types of adsorption, magnitude of adsorption (Γ), polarization potential (φ), zero charge potential (φ_0) and the types of additives, as it is shown in the diagram.

For all types of additives in the 1 and 1' regions electrochemical reactions take place, while the regions 2 and 2' and 3 are those where adsorption takes place. The boundaries between these regions are not stationary (they are determined by many factors which are not considered here), thus we show them with wavy lines.

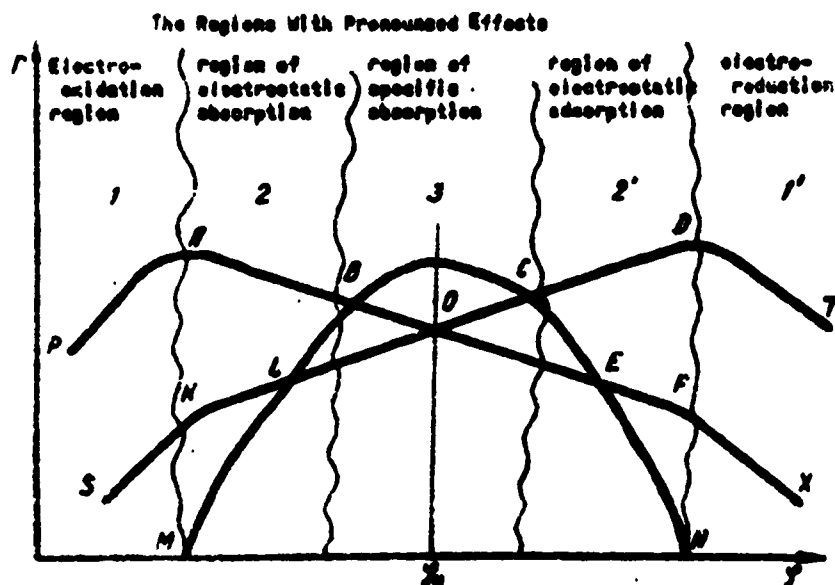


Fig. Typical Regions of the Adsorption Processes at the Electrodes Polarized by External Currents

In cathodic polarization the electrostatic adsorption of cations increases (curve KLOGD), and for anions it lowers (curve ABOEF). The specific action increases the adsorption independently of the nature of particles. Thus, if the additive is unchanged electrochemically the true adsorption curve for the additive of the cationic type will be MLEOD, while for the anionic type -- ABCEN. For such substances characteristic adsorption is absent at definite potentials (to the left and to the right of points M and N).

For additives which are electrooxidized or electroreduced the true adsorption shall be SKLEODT and PABOEFX respectively.

If the molecular substance does not change the zero charge potential then in moving away from the Φ_H to either side the specific adsorption decreases (region 3, curve BG). In the following change of the potential to either side a corresponding reorientation of polar molecules may occur, then the adsorption of substances increases as a result of electrostatic forces (CD and BA). The possibility is not excluded that oxidation or reduction of molecules may occur at further changes of potential (AP and DT). It is also possible that with the lowering of the action of the specific adsorption forces a desorption of molecular substances may begin, then

the curve for the molecules will follow the direction of GEN and BLM. A different path for the adsorption curves is also possible in which only one type of adsorption is predominant.

The scheme for visual representation of the relationship between types and magnitudes of adsorption, types of additives and polarization potential is cited.

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